



Rice stubble as a new biopolymer source to produce carboxymethyl cellulose-blended films

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ABSTRACT

Rice stubble is agricultural waste consisting of cellulose which can be converted to carboxymethyl cellulose from rice stubble (CMCr) as a potential biomaterial. Plasticizer types (glycerol and olive oil) and their contents were investigated to provide flexibility for use as food packaging material. Glycerol content enhanced extensibility, while olive oil content improved the moisture barrier of films. Additionally, CMCr showed potential as a replacement for up to 50% of commercial CMC without any changes in mechanical and permeability properties. A mixture of plasticizers (10% glycerol and 10% olive oil) provided blended film with good water barrier and mechanical properties comparable with 20% individual plasticizer. Principle component (PC) analysis with 2 PCs explained approximately 81% of the total variance, was a useful tool to select a suitable plasticizer ratio for blended film production. Therefore, CMCr can be used to form edible film and coating as a renewable environmentally friendly packaging material.

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1. Introduction

Biopolymer films have been explored recently due to their biodegradability and potential uses as an environmentally friendly packaging material. Polysaccharides are the main source of biopolymers, especially carboxymethyl cellulose (CMC) (Bifani et al., 2007; Mali, Grossmann, García, Martino, & Zaritzky, 2006). CMC is a water-soluble cellulose derivative which can be used alone or combined with other materials into an edible film; for example, CMC films blended with konjac glucomannan (Cheng, Karim, & Seow, 2008), modified starch (Ghanbarzadeh, Almasi, & Entezami, 2010) and corn starch (Kibar & Us, 2013).

Basically, CMC-based film provides a poor moisture barrier and poor mechanical properties, (brittleness) due to its hydrophilic character (Bifani et al., 2007; Petersson & Stading, 2005). Thus, plasticizers are required to overcome the film brittleness caused by intermolecular forces (Bifani et al., 2007). Glycerol is widely used to improve film flexibility and extensibility as it adds increased mobility of polymer chains (Bifani et al., 2007; Cao, Yang, & Fu,

2009; Mali et al., 2006). For example, glycerol increased the elastic modulus and elongation of CMC films (Ghanbarzadeh and Almasi, 2011). However, glycerol also increased the hydrophilicity of the film resulting in higher permeability (Ghanbarzadeh et al., 2010). Fatty acids, lipids, and vegetable oils have been incorporated as an emulsion film to increase water barrier effectiveness (Ma, Tang, Yin, Yang, Qi et al., 2012; Ma, Tang, Yin, Yang, Wang et al., 2012). Among vegetable oils, olive oil is an interesting source of monounsaturated fatty acids which has positive health benefits, especially natural antioxidants (López-Miranda, Pérez-Martínez, & Pérez-Jiménez, 2006) to improve the film water barrier as shown in whey protein film (Javanmard, 2008), gelatin-based films (Ma, Tang, Yin, Yang, Qi et al., 2012; Ma, Tang, Yin, Yang, Wang et al., 2012) and chitosan emulsion films (Pereda, Amica, & Marcovich, 2012). Therefore, it is useful to investigate the effect of olive oil in CMC-based films as to date, there is no information available on this topic. This will benefit not only improving the film properties but will also provide nutrition when the edible film is applied directly to food products.

Recently, renewable sources to obtain CMC have been continuously explored as biodegradable and edible films and coatings (Haq, Hasnain, & Azam, 2014; Ma, Tang, Yin, Yang, Qi et al., 2012). CMC from sugar beet pulp (Toğrul and Arslan, 2004) and CMC film from durian rind cellulose (Rachtanapun, Luangkamin, Tanprasert, & Suriyatem, 2012) are example. In Thailand, rice stubble constitutes a large amount of the agricultural waste residues left in the

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field after harvest and when they are burnt, there are undesirable effects on environmental pollution and human health. Rice stubble consists of mainly cellulose and to date, no study has synthesized CMC from rice stubble. Therefore, the successful synthesis of CMC from rice stubble may be a replacement for the commercial CMC used in the food industry which must be imported from other countries. Moreover, conversion into CMC will add value to local agricultural waste from rice production.

Thus, the aims of this work were: (i) to select the desirable concentration of each plasticizer (glycerol, olive oil, and mixture of glycerol and olive oil) for commercial CMC (CMC_c)-based films; and (ii) to study the feasibility of CMC from rice stubble (CMC_r) as a replacement of CMC_c and as a renewable source for biodegradable film and coating materials.

2. Materials and methods

2.1. Raw materials

Rice stubble (*Oryza sativa* cv. Khao Dawk Mali 105), residues in a local rice field (Ratchaburi, Thailand), was washed with tap water, cut into small pieces (0.1–0.5 cm long), and then dried in an hot air oven (RF 115, RedLINE, Germany) at 60 °C for 10 h.

Commercial carboxymethyl cellulose (CMC_c, CEKOL[®] 700 Cellulose gum, purity 99.5%, DS 0.75–0.85, molecular weight 270,000 Da) was donated from Winner Group Enterprise Plc. (Bangkok, Thailand). Extra light olive oil (BERTOLLI, Italy) was purchased from local supermarket. Generally, the total phenolic compounds and tocopherols were the main antioxidants presented in the extra light olive oil. All chemical reagents used were analytical grade. Glycerol and sodium hydroxide (NaOH) were purchased from Ajax Finechem Pty Ltd (New South Wales, Australia). Methanol, ethanol and chloroacetic acid (ClCH₂COOH) were purchased from Merck KGaA (Darmstadt, Germany). Sodium hypochlorite (NaOCl, food grade, 10%) was obtained from U&V Holding (Thailand) Co., Ltd. (Nonthaburi, Thailand). Isopropanol and glacial acetic acid were purchased from QRÉcTM (Auckland, New Zealand).

2.2. Synthesis of carboxymethyl cellulose from rice stubble (CMC_r)

The cellulose from rice stubble was previously isolated according to the method of Rodsamran and Sothornvit (2015). Briefly, dried rice stubble was boiled in distilled water for 30 min to remove dust and then filtered. The hemicellulose and lignin were removed using NaOH (10% w/w) at 55 °C for 3 h and NaOCl (5% v/v) at 75 °C for 15 min, respectively. Then, the residual cellulose was washed with distilled water and 95% ethanol before drying in a hot air oven at 60 °C for 8 h.

A sample of rice stubble cellulose (5 g) was swollen in a mixed solution of 25 mL of 30% w/w NaOH and 100 mL of isopropanol for 90 min. Chloroacetic acid (7 g) was added, stirred at room temperature (RT, 28 ± 2 °C) for 30 min and reacted at 50 °C for 180 min. After filtration, the mixture was soaked in 70% ethanol for 10 min and neutralized with 90% acetic acid. The CMC_r was washed with 70% methanol three times and then finally washed with absolute ethanol. Finally, CMC_r was dried in a hot air oven at 60 °C for 8 h, ground and kept in a polyethylene zip lock bag. Based on the ASTM D1439–03 method (ASTM, 2008), the degree of substitution (DS) and purity of CMC_r were 0.64 and 95%, respectively.

2.3. Plasticized-based film formation

CMC_c and CMC_r solutions were prepared by dissolving CMC (1%, w/v) in hot deionized water (70 °C) using a magnetic stirrer for 10 min and left overnight at RT to dissolve completely.

Table 1

Composition of commercial carboxymethyl cellulose (CMC_c)-based films.

Plasticizer	Treatment	Glycerol (% w/w CMC _c)	Olive oil (% w/w CMC _c)
No	Control	0	0
Glycerol (G)	G 10	10	0
	G 20	20	0
	G 30	30	0
Olive oil (OL)	OL 10	0	10
	OL 20	0	20
	OL 30	0	30
	OL 40	0	40
Mixture (G:OL)	G 5 OL 5	5	5
	G 5 OL 15	5	15
	G 5 OL 25	5	25
	G 10 OL 10	10	10
	G 10 OL 30	10	30

Plasticizers were added drop-wise into CMC_c solution or CMC_c/CMC_r-blended solution with continuous homogenization at 20,000 rpm for 20 min using a homogenizer (POLYTRON PT-MR 3100D, KINEMATICA AG, Luzern, Switzerland). Plasticized film solution was degassed in a vacuum and cast onto a polystyrene dish (58 cm²). The film thickness was controlled by the amount of solution (28 g). The film was dried in a hot air oven at 45 °C for 16 h, peeled and kept in a sealed polyethylene bag at 25 ± 3 °C, 50 ± 2% relative humidity (RH) until being used. Film thickness was measured using a micrometer (No.7326, Mitutoyo Manufacturing Co. Ltd., Tokyo, Japan).

2.3.1. Effect of plasticizer concentrations

Three plasticizer types (glycerol, G; olive oil, OL and a mixture of glycerol and olive oil defined by their ratio, G:OL) were added based on the CMC_c solution weight (Table 1). The film forming solution without plasticizer was used as the control film.

2.3.2. Effect of substitution with CMC_r

CMC_r solution (1%, w/v) was blended in CMC_c solution (1%, w/v) at the ratio of 0:100, 25:75, 50:50, 75:25 and 100:0 (v/v) to form plasticized-based films.

2.4. Characterization of films

2.4.1. Moisture content

The moisture content (MC) was measured according to AOAC methods (934.01 AOAC, 2002).

2.4.2. Film solubility

Film specimens were cut into 2 cm × 2 cm squares and dried at 105 °C in a hot air oven for 24 h. After drying, films were weighed to the nearest 0.0001 g to determine the initial dry weights of each sample. Films were individually placed into 20 mL of distilled water in glass tubes. The tubes were capped and placed in a shaking water bath at 25 ± 0.1 °C for 24 h. Film pieces were then taken out and dried at 105 °C in a hot air oven for 24 h to determine the final dry weight of films. Three replicates of each film were done. Solubility in water was calculated using Eq. (1):

$$\text{Solubility (\%)} = \frac{(\text{initial dry weight} - \text{final dry weight})}{\text{initial dry weight}} \times 100 \quad (1)$$

2.4.3. Film opacity

Film opacity was measured according to the method of Pereda et al. (2012) with some modification. Briefly, three rectangular strips (1 cm × 4 cm) were directly placed in the test cell of UV-vis spectrophotometer (UV 1800, Shimadzu, Tokyo, Japan). The absorption spectrum of the film sample was recorded from 200 to

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